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Investigations of Intercalation in Inorganic Solids with Layered Structures: Iron-57 Mössbauer Spectroscopy Studies of Size Fractionated and Iron-Exchanged Montmorillonite Clays

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Abstract

^{57}Fe Mössbauer spectroscopy has been used to examine some naturally occurring layer silicates in which cations located in exchange sites in the interlayer regions can be replaced by other species. The ^{57}Fe Mössbauer spectra recorded from differing size fractions of two types of non-exchanged and sodium-exchanged montmorillonite clays were found to be independent of the fraction size. The spectra have been interpreted in terms of the occupation by iron(III) of a heterogeneity of similar sites within the montmorillonite lattice. No justification has been obtained for computer analysis of the data in terms of more than one characterisable lattice site and no evidence has been found for the association of any iron oxyhydroxide impurity with the montmorillonite fractions.

The ^{57}Fe Mössbauer parameters recorded from iron(III)-exchanged montmorillonite, in which iron(III) species are intercalated within the layers, show that the process is best performed at fairly low pH using low concentrations of iron(III). Failure to control such conditions can result in the formation of iron oxyhydroxides or hydrolysed iron(III) species. The preparation of iron(II)-exchanged montmorillonite was accompanied by partial oxidation of the iron(II) to iron(III).

Introduction

Intercalation involves the reversible insertion of guest species into a lamellar host structure with the maintenance of the structural features of the host. The nature of inorganic host materials range from electrical insulators, such as molybdenum(VI) oxide, silicate clays and zeolites, through semiconductors such as graphite and transition metal dichalcogenides, to metallic conductors such as lanthanum nitride. The naturally occurring insulating layer silicates are host lattices with considerable current interest because of their potential technological applications [1]. We are currently developing a programme of work in intercalation chemistry in inorganic systems and, since the chemistry of the layer silicate materials is primarily dominated by the intercalation of neutral molecules and by ion exchange, we have performed initial studies on these types of materials. In particular, we have focussed attention on the intercalation of iron species within the layers since these can strongly coordinate neutral polar species with a concomitant expansion of the interlayer region [2].

Montmorillonite, one of the smectite group of expanding layer silicate minerals, is composed of aluminium ions in octahedral coordination sandwiched between two sheets of silicon ions in tetrahedral coordination [1]. These 2:1 layer units stack on top of each other to give clays in which the aluminium can be randomly substituted by cations of similar size such as magnesium(II) and, to a lesser extent, iron(III) and iron(II). The resulting charge deficit is distributed over the surface of the layers and is compensated by the intercalation of exchangeable hydrated cations which force the layers apart. Iron may therefore be associated with the clay either through isomorphous substitution within the lattice or as intercalated cations which, by neutralising the charge in the interlayer regions and clay surfaces, give rise to the formation of iron-exchanged clays.

Mössbauer spectroscopy is a technique which is well suited to the identification of iron in different oxidation states and in different locations such as within the lattice or within the layers. The initial studies of montmorillonite by Mössbauer spectroscopy reported the presence of iron(III) [3–10], sometimes in more than one site [5–7], and sometimes in combination with iron(II) [5–10]. More recent studies [11] have reported the occupation of the exchange sites by solvated iron(II) and, in iron(III)-exchanged clays, some iron(III). We report here on our investigations of iron in natural and

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TABLE I. Iron-57 Mössbauer Parameters Recorded from Montmorillonite of Differing Particle Sizes

Sample		Temperature of Mössbauer measurement (K)	$\delta \pm 0.01$ (mm s^{-1})	$\Delta \pm 0.02$ (mm s^{-1})
Non-exchanged STx-1 unfractionated		298	0.25	0.46
		77	0.45	0.60
	1–2 μ	298	0.22	0.46
	0.5–1 μm	77	0.41	0.49
	<0.05 μm	298	0.20	0.43
Na^+-exchanged STx-1 unfractionated		298	0.15	0.49
	1–2 μm	298	0.16	0.43
	<0.5 μm	298	0.17	0.50
		77	0.29	0.38
Non-exchanged SWy-1	0.5–1 μm	298	0.29	0.33
		77	0.37	0.57
Na^+-exchanged SWy-1	0.5–1 μm	77	0.46	0.54

size-fractionated montmorillonite and of iron(II)- and iron(III)-exchanged montmorillonite by iron-57 Mössbauer spectroscopy.

Experimental

The Clay Minerals Society montmorillonite 'source clays' STx-1 and SWy-1 containing 0.56% and 2.60% iron respectively were sodium-exchanged using 1 M sodium chloride solutions and, after dialysing to remove excess sodium ions, the <2 μm fraction was removed by sedimentation. This fraction was subdivided into 1–2 μm, 0.5–1 μm, 0.05–0.5 μm and <0.05 μm fractions by centrifugation. All the fractions were freeze dried.

Iron-exchanged montmorillonites were prepared under gaseous nitrogen by similar methods to those described elsewhere [10]. The iron(II)-exchanged montmorillonites were obtained by adding iron(II) chloride tetrahydrate, $FeCl_2 \cdot 4H_2O$, containing 1000 μeq g^{-1} Fe(II) in water (10 dm^3) to the sodium-exchanged clay (0.2 g). In some cases the pH was adjusted to 1.8 by the addition of dilute hydrochloric acid. The suspensions were shaken (1 h), centrifuged, the supernatant liquids removed, and the sediments washed with water, or in the case of the pH adjusted samples with 0.005 M hydrochloric acid, before freeze drying. Iron(III)-exchanged montmorillonites were prepared by a similar method from iron(III) nitrate nonahydrate, $Fe(NO)_3 \cdot 9H_2O$. Some of the preparations were performed at pH 1.0 using dilute hydrochloric acid to adjust the pH.

Aqueous solutions of the iron(II) and iron(III) salts were also added to silica which had been pretreated with dilute sodium hydroxide to remove superficial silicic acid. The iron(II)- and iron(III)-treated silica samples were freeze dried as in the case of the montmorillonite preparations.

Iron-57 Mössbauer spectra were recorded at 298, 77 and 4 K from samples containing less than 50 mg iron cm^{-2} with a Cryophysics MS-102 microprocessor controlled Mössbauer spectrometer using a 25 mCi $^{57}Co/Rh$ source at 298 K. All the spectra were computer fitted and the chemical isomer shift data quoted relative to metallic iron.

Results and Discussion

Size Fractionated Montmorillonite

The ^{57}Fe Mössbauer parameters recorded from STx-1 and SWy-1 fractions of differing sizes are recorded in Table I. All the spectra showed quadrupole split absorptions characteristic of high spin iron(III) in a distorted octahedral environment. It is pertinent to note that the spectra recorded from the sodium-exchanged montmorillonites, in which external surface and interlayer iron species had been removed, were not significantly different from the spectra recorded from the non-exchanged materials, hence it appears tha the quadrupole split absorptions recorded from all the fractions may be associated with the iron(III) in the montmorillonite lattice.

The linewidths of the Mössbauer spectral peaks, *ca.* 0.48 to 0.78 mm s^{-1}, were broader than those observed [12] in the spectra recorded from iron(III) in silicate minerals, *ca.* 0.35 mm s^{-1}. Given the random nature of the isomorphous substitution of iron within the octahedral sites the somewhat broad linewidths may be associated with the occupation by iron of a heterogeneity of similar sites which give rise to the superposition of similar quadrupole split absorptions.

Although the quadrupole split, ^{57}Fe Mössbauer spectra recorded from montmorillonite clays have, in the past, sometimes been fitted to two partially superimposed doublets and interpreted in terms of the

TABLE II. Iron-57 Mössbauer Parameters Recorded from Iron-Exchanged Montmorillonite and from Iron Salts Supported on Silica

Sample	pH of medium during iron exchanging	Temperature of Mössbauer measurement (K)	Assignment	$\delta \pm 0.01$ (mm s^{-1})	$\Delta \pm 0.02$ (mm s^{-1})
Na$^+$-exchanged SWy-1		77	lattice Fe(III)	0.46	0.54
Iron(II)-exchanged SWy-1	1.8	77	lattice/exchange Fe(III)	0.41	0.44
			exchange Fe(II)	1.45	3.28
	4.4	77	Fe(III)A	0.48	0.54
			Fe(III)B	0.51	1.01
			exchange Fe(II)	1.40	3.36
		4	Fe(III)A	0.47	0.48
			Fe(III)B	0.52	0.99
			exchange Fe(II)	1.45	3.44
Iron(III)-exchanged SWy-1	1.0	77	Fe(III)A	0.49	0.55
			Fe(III)B	0.73	2.15
	2.5	77	Fe(III)A	0.50	0.66
			Fe(III)B	0.59	1.66
		4	Fe(III)A	0.50	0.60
			Fe(III)B	0.58	1.75
Silica treated with $FeCl_2 \cdot 4H_2O$		77	Fe(III)	0.66	0.65
			Fe(II)	1.25	2.59
Silica treated with $Fe(NO_3)_3 \cdot 9H_2O$		77	Fe(III)	0.48	0.60

occupation by lattice ion of two types of site of slightly differing symmetry [5–7], computer analysis of the data recorded from the fractions examined here failed to justify the fitting of the spectra to more than the single quadrupole split absorption associated with iron(III) within the montmorillonite lattice.

The most striking implication of the data in Table I is that the Mössbauer parameters are independent of the size of the montmorillonite fraction. The results are therefore consistent with the demonstrated similarity in chemical composition of different montmorillonite size fractions [13].

The absence of magnetic hyperfine splitting in the ^{57}Fe Mössbauer spectra recorded at 77 K, particularly from the smallest size montmorillonite fractions where the proportion of any iron-oxides or -oxyhydroxides bound to the clay surface would be expected to be greatest, suggests that any α-FeOOH or β-FeOOH which may be associated with the montmorillonite phase [14] is either below the level of detectability of ^{57}Fe Mössbauer spectroscopy or that it is of very small particle size such that the material is superparamagnetic. The failure of the ^{57}Fe Mössbauer spectra recorded from iron(II)- and iron(III)-exchanged montmorillonite at 4 K, *i.e.* below the Néel temperature of 73 K at which γ-FeOOH orders, to show any evidence of magnetic hyperfine splitting is consistent with the absence of significant concentrations of FeOOH in the materials examined here.

Iron(II)- and Iron(III)-Exchanged Montmorillonite

The ^{57}Fe Mössbauer spectra recorded from some of the iron-exchanged montmorillonite clays could be fitted to two partially superimposed doublets which are characteristic of iron(III) and designated as Fe(III)A and Fe(III)B (Fig. 1). The ^{57}Fe Mössbauer parameters recorded from the iron-exchanged montmorillonites and from silica when treated with aqueous solutions of the iron salts are recorded in Table II.

The Mössbauer spectrum recorded at 4 K from the iron(III)-exchanged montmorillonite prepared at pH 2.5 (Fig. 1b) was fitted to two quadrupole split absorptions characteristic of iron(III). The doublet described as Fe(III)A has ^{57}Fe Mössbauer parameters which are similar to those recorded from the sodium-exchanged SWy-1 montmorillonite suggesting that the absorption is, at least in part, a reflection of iron(III) in the lattice. However, since the Mössbauer parameters are also similar to those recorded from freeze dried silica following treatment with an aqueous solution of iron(III) nitrate it would appear likely that the Fe(III)A absorption also represents the iron(III) which has exchanged with exchangeable sodium ions. The quadrupole splitting of the Fe(III)B component of the spectrum exceeds that reported [5] for the larger quadrupole split absorption in the Mössbauer spectrum recorded from sodium-exchanged montmorillonite and interpreted in terms of iron(III) in the more distorted of two types of lattice

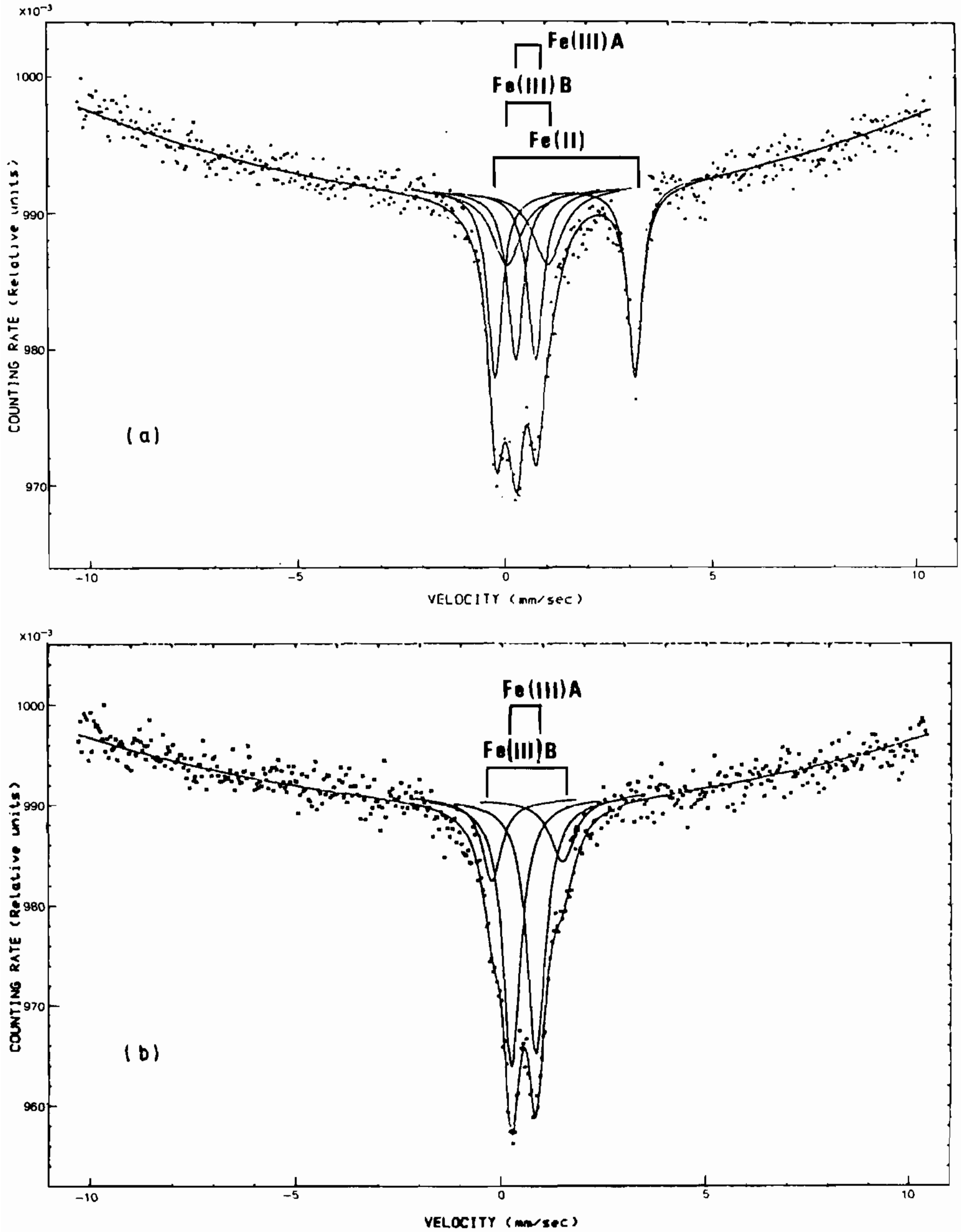

Fig. 1. Iron-57 Mössbauer spectra recorded at 4 K from: (a) iron(II)-exchanged SWy-1 montmorillonite prepared at pH 4.4, (b) iron(III)-exchanged SWy-1 montmorillonite prepared at pH 2.5.

sites and which is the subject of some uncertainty (*vide supra*). Furthermore, the absence of any magnetic hyperfine splitting in the Mössbauer spectrum of the iron(III)-exchanged montmorillonite recorded at 4 K suggests that the Fe(III)B doublet is not the result of small particle superparamagnetic iron oxyhydroxides such as β-FeOOH [11]. However, the doublet, which is characteristic of iron(III) in a highly distorted environment, is similar to that which has been associated [11] with species such as $FeCl^{2+}$(aq) and $Fe(OH)^{2+}$(aq) which can form when montmorillonite is treated with iron(III)-containing solutions during iron exchanging processes. The absence of such a component in the Mössbauer spectrum recorded from silica following its treatment with iron(III)-containing solutions would suggest that any formation of species such as $FeCl^{2+}$(aq) and $Fe(OH)^{2+}$(aq) during iron-exchange procedures, and which is reflected in the Fe(III)B component of

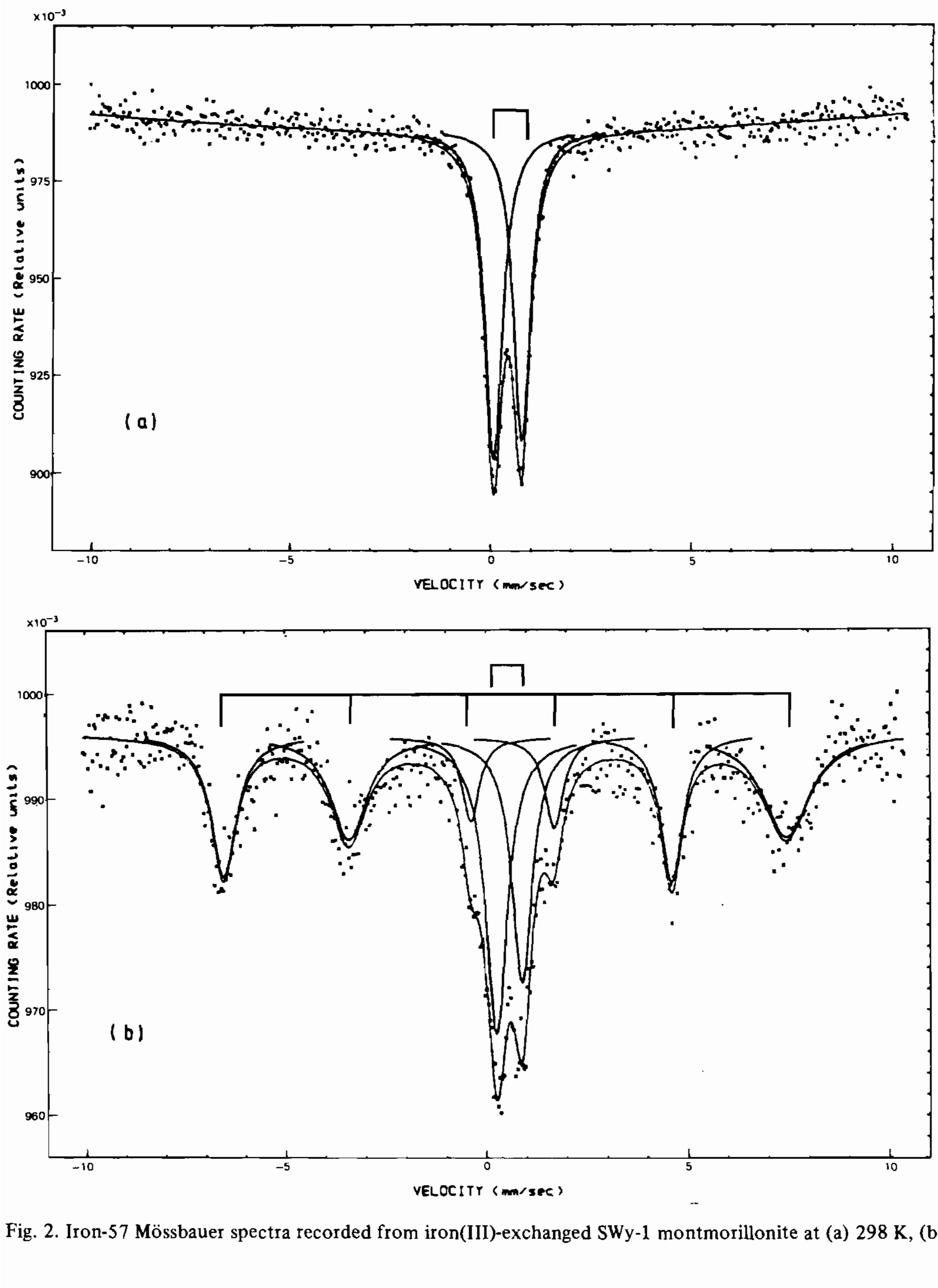

Fig. 2. Iron-57 Mössbauer spectra recorded from iron(III)-exchanged SWy-1 montmorillonite at (a) 298 K, (b) 77 K.

the spectrum, is also related to the nature of montmorillonite itself.

The ^{57}Fe Mössbauer spectrum recorded at 4 K from iron(II)-exchanged SWy-1 montmorillonite prepared at pH 4.4 (Fig. 1a) showed three quadrupole split absorptions. The doublet with the largest quadrupole splitting is characteristic of high-spin iron(II) whilst the other two doublets may be associated with the two high spin Fe(III)A and Fe(III)B species arising, at least partially, from the inevitable oxidation of some of the iron(II). The presence of iron(III) was also observed in the Mössbauer spectrum recorded from silica following treatment with an iron(II)-containing solution. The iron(II) component in the Mössbauer spectrum recorded at 77 K was less intense than that in the spectrum recorded at 4 K as a result of the lower recoil-free fraction of the iron(II) species which is weakly bound in the interlayer region of the montmorillonite structure.

Although the ^{57}Fe Mössbauer spectra recorded from iron-exchanged montmorillonites prepared at pH 1.8 or 1.0 showed a diminuation, or even absence, of the Fe(III)B component, it is interesting to note that where the Fe(III)B component was evident the quadrupole splitting was significantly larger than that associated with Fe(III)B in the iron-exchanged montmorillonites prepared at pH 4.4 or 2.5. Given that leaching of aluminium(III) from the montmorillonite lattice by acid is well-known [15–17], it is reasonable to expect that iron(III) might be mobilised in a similar way at low pH and perhaps be associated with the formation of entities such as $FeCl^{2+}$(aq) and $Fe(OH)^{2+}$(aq) in highly distorted environments. However, the ^{57}Fe Mössbauer spectra recorded from the <2 μm sodium-exchanged SWy-1 montmorillonite following treatment with various concentrations of hydrochloric acid for periods between 4 h and 24 days failed to show significant increases in quadrupole splitting as might be expected if such treatments had leached iron(III) from the lattice to produce $FeCl^{2+}$(aq) or $Fe(OH)^{2+}$(aq) species. Given that the infrared spectrum recorded from the sodium-exchanged montmorillonite was similar to that recorded following treatment of the material in hydrochloric acid, it seems that any leaching of iron(III) from the montmorillonite lattice by hydrochloric acid is minimal.

It is also pertinent to mention that when an iron(III)-exchanged montmorillonite was prepared from an excess of hydrated iron(III) chloride by methods analogous to those used to prepare sodium-exchanged clays, the ^{57}Fe Mössbauer spectrum recorded at 298 K (Fig. 2a) showed a quadrupole split absorption characteristic of high spin iron(III) whilst the spectrum obtained at 77 K (Fig. 2b) consisted of the superposition of the doublet on a sextet pattern similar to that recorded from small particle iron-oxides and -oxyhydroxides which only magnetically order at low temperature [18]. Although the broad linewidths and irregular shapes of the Mössbauer absorptions precluded accurate analysis of the magnetic interactions, the spectrum did allow an estimate of *ca.* 458 kG to be associated with the magnetic splitting, and the spectrum therefore has similarities with that reported [19] for β-FeOOH. Although the ^{57}Fe Mössbauer parameters for different iron-oxides and -oxyhydroxides are very similar [18], it is relevant to note that iron(III) within the montmorillonite lattice gives a quadrupole split Mössbauer spectrum (*vide supra*) and that the magnetic hyperfine pattern recorded at 77 K from the red–brown iron(III)-exchanged montmorillonite may be associated with the presence of iron-oxides or -oxyhydroxides at the clay surface and/or within the interlayer regions.

Hence iron(III)-exchanging of montmorillonite would appear to be best performed using dilute solutions of iron(III) salts at low pH values. A failure to control such conditions may result in the formation of oxyhydroxide structures. Indeed, the formation of hydrolysed iron(III) species such as $FeCl^{2+}$(aq) and $Fe(OH)^{2+}$(aq) when iron exchanging is performed even at low pH and at low iron concentration may represent the first stages in the formation of the iron oxyhydroxides which are frequently observed in iron(III)-exchanged montmorillonites.

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